

University of Groningen

The FT-IR studies of the interactions of CO₂ and polymers having different chain groups

Nalawade, SP; Picchioni, F; Marsman, JH; Janssen, LPBM; Nalawade, Sameer P.

Published in:
Journal of Supercritical Fluids

DOI:
[10.1016/j.supflu.2005.06.005](https://doi.org/10.1016/j.supflu.2005.06.005)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2006

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Nalawade, SP., Picchioni, F., Marsman, JH., Janssen, LPBM., & Nalawade, S. P. (2006). The FT-IR studies of the interactions of CO₂ and polymers having different chain groups. *Journal of Supercritical Fluids*, 36(3), 236-244. <https://doi.org/10.1016/j.supflu.2005.06.005>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

The FT-IR studies of the interactions of CO₂ and polymers having different chain groups

Sameer P. Nalawade*, F. Picchioni, Jan H. Marsman, L.P.B.M. Janssen

Department of Chemical Engineering, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Received 13 January 2005; received in revised form 3 June 2005; accepted 15 June 2005

Abstract

A Fourier transform-infrared spectroscopy (FT-IR) set up has been successfully modified in order to characterize different polymeric materials under sub- and supercritical CO₂ conditions. Polymers used in this study are polyesters (P120 and P130), poly(ethylene glycol) (PEG) and polyphenylene oxide (PPO). Analysis of the corresponding spectra shows evidences of weak interaction (Lewis acid–base) between CO₂ and polymers. In particular, shifts to higher wavelengths of the maximum absorption of chain groups of the polymer and the modification of the absorption band of CO₂ represent a qualitative evidence of such interactions. Analysis of CO₂ absorption bands allowed ranking of the polymeric materials according to interaction strength with CO₂. In general, polymers with ether group display higher interaction strength than polyesters. The effect of the dissolved CO₂ on the depression of the melting point, T_m or the glass transition temperature, T_g can also be studied using the FT-IR depending on the enhancement in the free volume. The shape of the spectrum in PEG, unlike the other polymers, was completely modified above the critical pressure (7.38 MPa).

© 2005 Elsevier B.V. All rights reserved.

Keywords: FT-IR; CO₂; Polyesters; Poly(ethylene glycol); Polyphenylene oxide

1. Introduction

Nowadays, CO₂ has become a potential solvent for various polymer applications in polymer processing as well as polymer synthesis [1–3]. An inert nature and a low cost due to its abundance in the atmosphere are the most attractive advantages of CO₂ as a solvent. The dissolved CO₂ in a polymer reduces the viscosity and allows the process or the synthesis to be carried out at a lower temperature. It makes the process or the synthesis less energy consumptive. In the applications, the solubility of CO₂ in a polymer is the vital parameter for its selection as a solvent. The higher the solubility of CO₂ in a polymer, the higher is the reduction in the viscosity. The solubility represents the amount of the CO₂ that can be dissolved at equilibrium conditions. The solubility measurement data of various polymer–CO₂ systems are well described in the literature [3]. The available data have mostly been interpreted

thermodynamically in terms of the effect of temperature and pressure on the solubility of CO₂ in a polymer.

Earlier, it was a general notion that the CO₂ solubility in a polymer is a function of pressure and temperature only. In fact, the amount of dissolved CO₂ varies from one polymer to another even at the same conditions. The specific intermolecular interaction between CO₂ and polymer is responsible for the different solubility. The nature of interaction present between CO₂ and a polymer is mostly of a Lewis acid–base kind. Fourier transmission infrared spectroscopy (FT-IR) is a powerful tool to study such interactions [4–11]. Albeit CO₂ lacks a dipole moment, it has a large quadrupole moment and both Lewis acid and base sites. In CO₂, a Lewis acidity results from the electropositivity of the carbon atom due to deficiency of electron density compared to the oxygen atoms. Thus, an electron acceptor–donor interaction is present when CO₂ is contacted with a polymer containing Lewis base sites. Few authors have revealed the specific intermolecular interactions between CO₂ and different polymers by carrying out IR spectroscopy studies.

* Corresponding author. Tel.: +31 50 363 4462; fax: +31 50 363 4479.
E-mail address: s.p.nalawade@rug.nl (S.P. Nalawade).

The FT-IR spectra of cellulose acetate (CA) and poly(methyl methacrylate) (PMMA) in the presence and the absence of CO₂ were recorded by Fried and Li [4]. In the study, the carbonyl stretching vibrations for CA and PMMA were shifted to higher wavenumbers in the presence of CO₂. Since the observed shifts were rather small, dipole–dipole interactions between the CO₂ and the carbonyl groups were suggested instead of the Lewis acid–base interactions. Later on, Kazarian et al. [6,7] also used FT-IR to study the intermolecular interactions between CO₂ and polymers. They used the bending mode (ν_2 , around 660 cm⁻¹) of CO₂ to show the interactions with the polymers. In case of polymers containing carbonyl group, e.g. PMMA, splitting of the ν_2 was observed. The splitting is due to the Lewis acid–base interaction where the carbonyl group act as an electron donor and CO₂ act as an electron acceptor. No such splitting has been reported for the polyethylene (PE) and polystyrene (PS). The reason is the absence of carbonyl group in PS as well as PE. However, some distortion of the ν_2 was observed only in PS. This is due to the interaction between CO₂ and the phenyl ring in PS. Meredith et al. [8] also used FT-IR spectroscopy to test the intermolecular interaction of CO₂ with different Lewis bases: triethylamine (TEA), pyridine (PYR), and tributyl phosphate (TBP). In case of PYR, a base having phenyl ring, no splitting was observed similar to PS and PE. Recently, both the antisymmetric stretching mode (ν_2) and the ν_2 of CO₂ were used to show the intermolecular interaction between PMMA, PS or polycarbonate (PC) [12]. The recorded spectra for the ν_2 of CO₂ in case of PMMA and PS has shown similar results, as explained earlier. In case of the ν_2 of CO₂ for PMMA and PC, an absorption band having a weak shoulder appeared in the spectra. The width of the absorption band was larger in PC compared to PMMA. Both the carbonyl groups as well as the benzene rings present in PC provide more sites for CO₂ molecules as compared to PMMA. In PS the recorded absorption band was not comparable, in terms of width, to those observed for PMMA and PC. In PS, the interactions are present only between CO₂ and the aromatic rings. These interactions are weaker than the ones present between CO₂ and carbonyl groups in PMMA and PC.

In this study, we have modified a golden gate FT-IR setup, generally used at an ambient pressure, to a high pressure FT-IR setup. The main aim of the study is to reveal the intermolecular interactions between CO₂ and polymers having different chemical groups along the main chain. The chemical groups, which are studied here include ester, ether and aromatic ring. The CO₂ bending mode has been studied for all the polymers to reveal the interactions as significant changes can be expected in it due to Lewis acid–base nature.

2. Experimental

2.1. Materials

Propoxy based (P120) and ethoxy based (P130) polyester (CAS:177834-94-5 and 170831-75-1) resins having molec-

Table 1
Glass transition temperatures of different polymers

Polymers	T_g or T_m (K)
P120	327.15
P130	330.15
PEG	331.15
PPO	503.15

ular weights: Mw-7000 and Mw-20000 were supplied by Akzo Nobel, The Netherlands. Chloroform (CHCl₃) and poly(ethylene glycol) (PEG) having Mw-6000 were purchased from Aldrich, The Netherlands. Polyphenylene oxide (PPO) of Mw-20000 was supplied by GE Corporations, The Netherlands. Glass transition temperature or melting points (T_g or T_m) of the polymers are provided in Table 1. High purity CO₂, 99.99%, was used in the FT-IR experiments. The materials were used without any purification treatment.

2.2. Apparatus

2.2.1. A low pressure FT-IR set up

For spectroscopic measurements in the presence of CO₂, the existing FT-IR golden gate apparatus was modified to a high pressure FT-IR set up. The golden gate apparatus is generally used to record spectra of a solid or molten material, which is usually provided in the form of a film or powder. Due to better uniformity a film rather than powder is preferred. The film is kept on the surface of the crystal (Quartz) mounted in the heating plate in conjunction with a temperature controller. The temperature of the material is raised using a heating plate in order to record the spectra of a molten or solid material. The maximum temperature to which crystal can be heated is 473.15 K. For the better contact of the solid film with the crystal, a groove–bolt arrangement is provided to apply a certain force on the film. The CO₂ absorbance becomes too high at higher pressures if the crystal of long path length is selected. Therefore, the ATR (attenuated total reflection) IR spectroscopy with FT-IR transmission was used in the study. The ATR spectroscopy provides the path length of only several micrometers [13].

2.2.2. Modified FT-IR set up

The schematic of the high pressure FT-IR unit is shown in Fig. 1. The high pressure unit consists of a golden gate FT-IR apparatus (Spectrum 2000, Perkin-Elmer, UK), the CO₂ cylinder, a high pressure syringe pump (Isco, USA), a high pressure cell and valves. The high pressure cell, tubes and valves are made of stainless steel. The high pressure cell was built up in the group, University of Groningen (The Netherlands). The same groove–bolt arrangement was used to ensure the good contact of an O-ring with the cell as well as the surface. The O-ring between the cell and the surface of the plate makes the system completely leak-proof. Using the groove–bolt arrangement the force is transferred from the cell to the O-ring by tightening the bolt. The cell can withstand pressures up to 10 MPa. CO₂ inlet and exit lines are

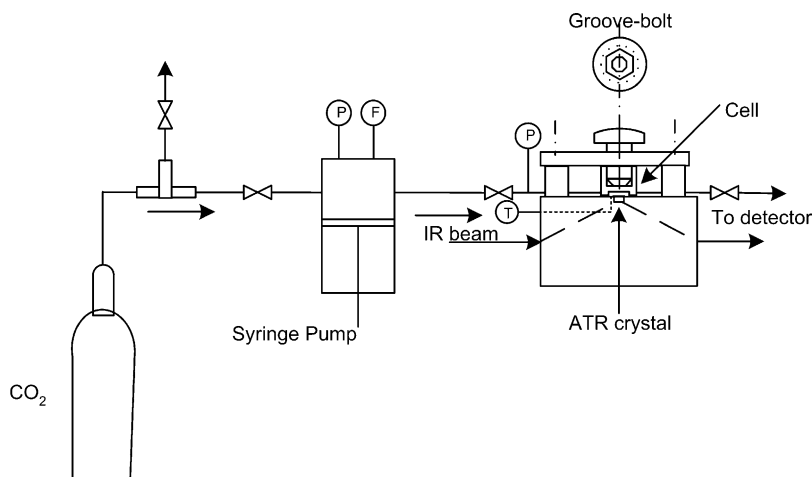


Fig. 1. The high pressure FT-IR golden gate unit.

provided along with the needle valves. The cell, inlet, exit lines and valves were completely insulated with a glass wool to prevent heat loss to the surrounding. The heating source was sufficient to raise the temperature of a polymer film as well as gas to a desired value as the internal volume of the cell was very small. To measure a pressure value, a bourdon pressure gauge meter was connected in between the CO₂ inlet line and the cell. The pressure gauge meter (Swagelok, Germany) can measure a pressure in bar ($P_{\max} = 10$ MPa). The spectra were measured on the Spectrum 2000 spectrometer. The scanning range available in the FT-IR set up is 500–4000 cm⁻¹.

2.3. Film preparations

The polymers were used in the form of a thin film. Different procedures were adopted to prepare thin films of polymers. Very small amounts of polymers were used for the film preparation. The use of organic solvent in the production of films was avoided whenever possible. In case of polyester resins and PEG, the films were prepared without using a solvent. The films were prepared directly on the crystal by melting the polyester resins and PEG. To obtain the molten polymer, the temperature of the crystal was raised above T_g or T_m . The molten polymer was then smeared as a very thin film using a thin glass slit. The film was then pressed against the crystal using the groove-bolt arrangement having a flat glass surface attached at the bottom of the nut. It ensures a uniform surface and a good contact of the film with the crystal. The thin film adheres to the surface of the crystal as it cools down. Since the T_g of PPO is very high, the above method was not suitable. A solvent cast method was used for PPO. A dilute solution of PPO and CHCl₃ was cast on a glass plate and kept in a vacuum oven at 318.15 K for three days to obtain a dried film. As PPO cannot be molten at a lower temperature, the film was pressed against the crystal using the flat surface attached at the bottom of the nut.

2.4. Experimental procedure

The cell and the polymer film were heated to a desired temperature. The spectra were recorded for the polymer film in an absence of CO₂. The cell was then flushed with CO₂ for 5–10 min using a syringe pump and keeping the valves open. After this, the desired pressure in the system was achieved by adjusting the flow rate in the pump and closing the exit valve. The inlet valve was closed as soon as the desired pressure in the cell was achieved. The system was kept under an isobaric and isothermal condition for at least 3 h. After recording the spectrum, the pressure was increased to a higher value. Sufficient time (less than 3 h) was provided for the CO₂ dissolution before recording the new spectrum. The spectra were scanned for the complete range with the resolution of 2 cm⁻¹. The average number of scans was 200. The spectra were recorded on a computer using the software, Spectrum for Windows, provided along with the FT-IR set up. The peak positions, as reported for each spectrum are taken in correspondence of the maximum absorption.

3. Results and discussion

3.1. PPO

The FT-IR experiments for PPO were carried out at 313.15 K. The spectra were recorded in the absence of CO₂ and at different CO₂ pressures (3–8 MPa) under an isothermal condition. In PPO, the CO₂ interactions are possible with the ether group as well as the aromatic ring. The effect of the dissolved CO₂ on the stretching vibrations of C–O group (sigma bond, ~1180 cm⁻¹) and the aromatic out-of plane bending vibrations of C–H (~855 cm⁻¹) [14] can be seen in Figs. 2 and 3, respectively.

From Figs. 2 and 3, it is clear that the C–O (sigma bond) stretching vibrations and aromatic C–H bending vibrations

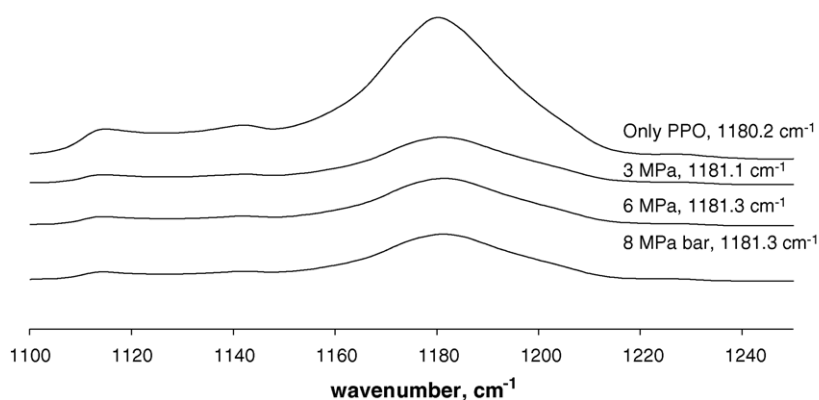


Fig. 2. The spectra of the stretching vibrations of C–O group (sigma bond) of PPO at 313.15 K.

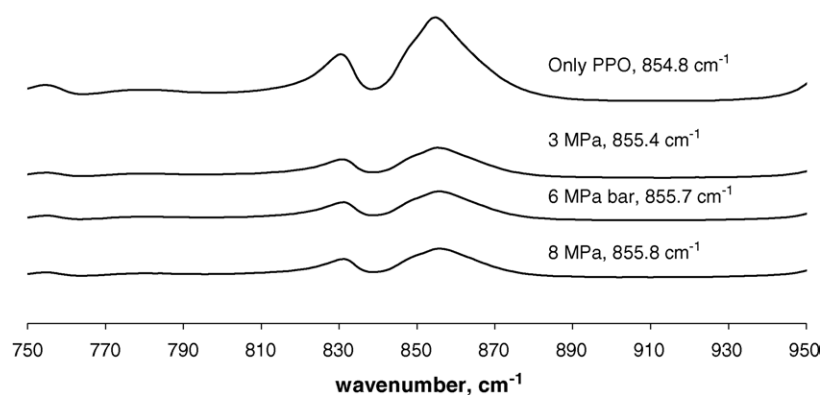


Fig. 3. The spectra of the out-of-plane bending vibrations of C–H group (aromatic ring) of PPO at 313.15 K.

were shifted slightly to higher wavenumbers in presence of CO₂. The wavenumber was shifted to higher values with the increasing CO₂ pressures in case of the ether as well as aromatic group. The shifts are attributed to the complexes formed

between CO₂ and the above mentioned groups. Actually, the evidence of interaction between CO₂ and the polymer can be visualized also in terms of the bending vibration of CO₂ as shown in Fig. 4. An extra band around 655 cm⁻¹ was

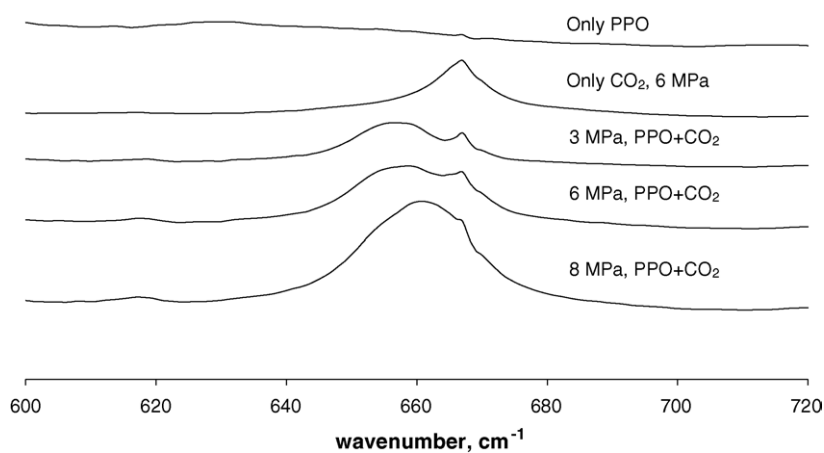


Fig. 4. The spectra of the bending vibrations of CO₂ entrapped into PPO at 313.15 K.

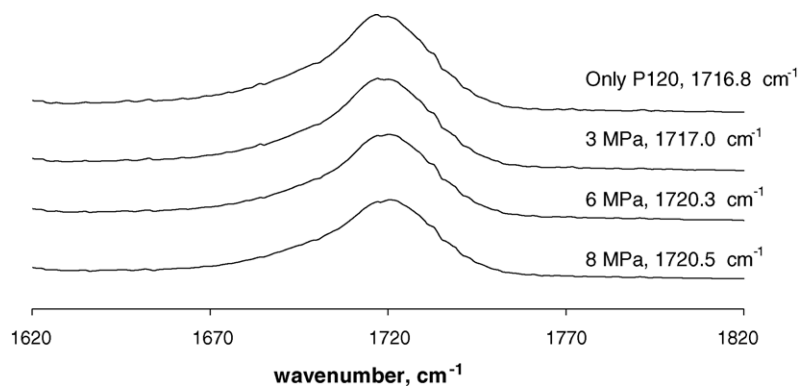


Fig. 5. The spectra of stretching vibrations of C=O group in P120 at 313.15 K.

observed for PPO in the presence of CO₂ compared to the single-band observed for CO₂ only at 667 cm⁻¹. This is in a full agreement with what reported earlier in the literature [7,8].

3.2. P120 and P130

In case of aromatic polyesters, the chemical groups that most probably interact with the CO₂ are the carboxyl one and the aromatic ring as before. Figs. 5 and 6 present the absorption profiles relative to the stretching vibration of the carboxyl group (C=O, around 1720 cm⁻¹ [15]) in P120 and P130 for various CO₂ pressures. The wave numbers were shifted to higher values, maximum shifts of 3.7 (P120) and 2 cm⁻¹ (P130). The shifts, in case of C=O, are in agreement with the strength of the interaction predictable on the basis of the chemical structure and with the data reported in the literature over the comparison of PMMA (4 cm⁻¹) [4,7]. While, in the region of the aromatic absorption (730 cm⁻¹ [15]) relatively lower shifts of 1.2 cm⁻¹ (maximum) are observed for both materials (only P120 is reported in Fig. 7).

Also, in this case modification of the CO₂ bending vibration (Fig. 8 for P120) can be observed along with the free CO₂ at 667 cm⁻¹. It clearly indicates the presence of interac-

tions of CO₂ with the Lewis base sites and the phenyl rings available in P120.

3.3. PEG

In PEG, the ether (C–O) group is able to interact with CO₂. When CO₂ was absorbed into PEG, a shift in the C–O stretching vibration [16,17] was observed. Albeit the shifts were smaller at sub-critical pressures, a complete modification in the shape of the spectrum was observed at a supercritical pressure (Fig. 9). This effect can be related to the enhancement in the free volume in the presence of CO₂. For PEG at 8 MPa the spectrum observed is representing the absorption bands of the polymer much closer to its *T_m*. This is in agreement with the thermal properties of PEG reported in the literature and namely with the *T_m* reduction of approximately 2 K/MPa (starting *T_m* of about 331.15 K) [18]. While in case of PPO, which also contains C–O group, the starting value of *T_g* (503.15 K) is too high to observe such effect on the shape of the spectrum (reduction of *T_g* for PPO is reported to be 5 K/MPa [3]).

Indeed, also the bending vibration of CO₂ entrapped in PEG (Fig. 10) displays a completely different spectrum with a very broad absorption at 8 MPa compared to what observed

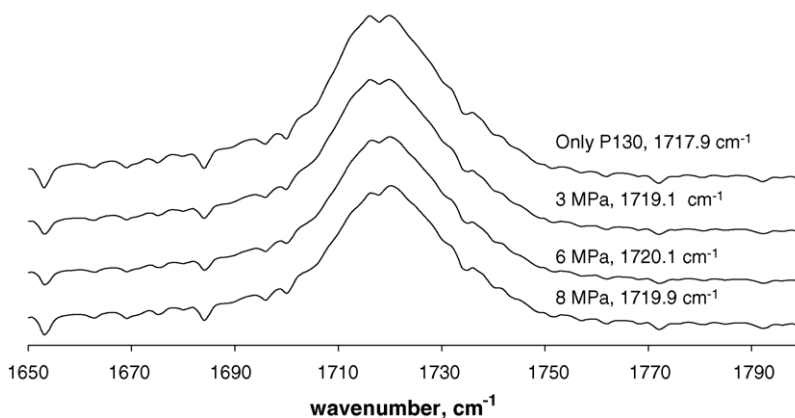


Fig. 6. The spectra of the stretching vibrations of C=O group in P130 at 313.15 K.

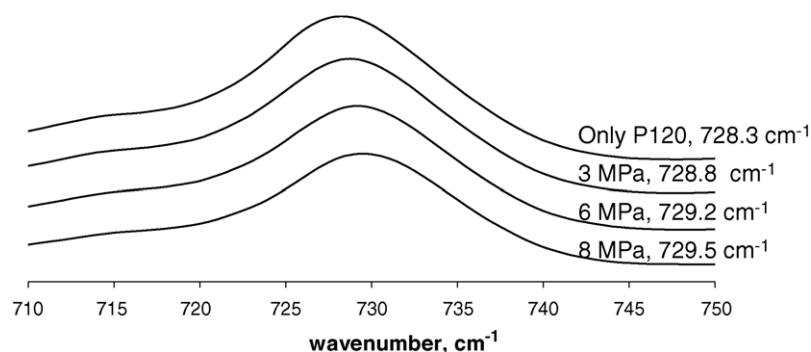


Fig. 7. The spectra of the out-of-plane bending vibrations of in the aromatic region of P120 at 313.15 K.

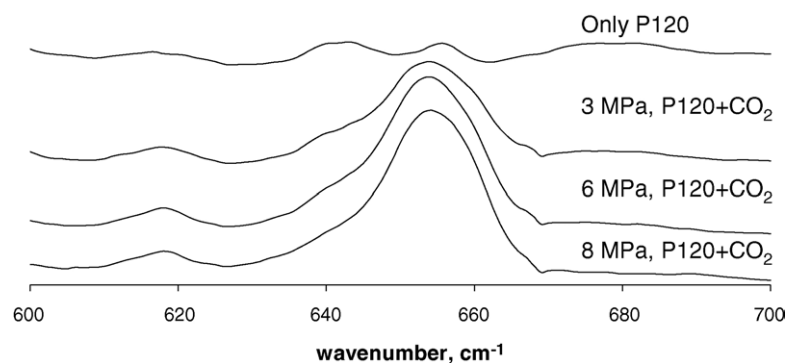


Fig. 8. The spectra of the bending vibrations of CO₂ entrapped into P120 at 313.15 K.

for the other polymers (Figs. 4 and 8). At 3 MPa, a relatively small, but broad, peak was observed. At 6 MPa, it was possible to observe the distinguished splitting of a band around 660 cm⁻¹ due to weak interactions between CO₂ and the ether group. Such splitting has already been reported in case of polymers not containing aromatic rings [7].

3.4. Discussion

Possible factors that can influence the shift of chemical groups present in the polymer as a function of CO₂ pressure

are: kind of chemical group, steric hindrance at the interaction site and an accessible free-volume.

The polymers studied in this work have in common the presence of chemical groups with the same structure. Upon interaction with CO₂, the IR absorption characteristic of every single group shifts to a higher wavelength, as already reported for Lewis acid–base kind of interaction. To our knowledge, no attempt is described in the literature in order to correlate the observed shift with the kind of polymer used. We have also tried to find a correlation by taking into account the most similar materials, i.e. P120 and P130.

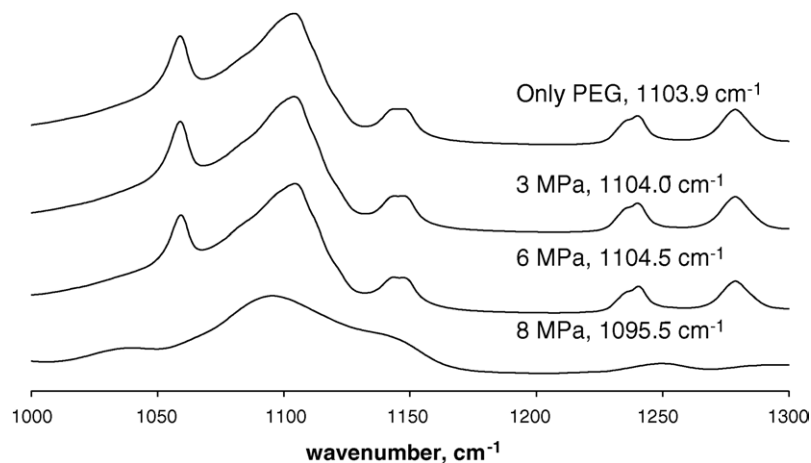


Fig. 9. C–O stretching vibration in PEG at different CO₂ pressures.

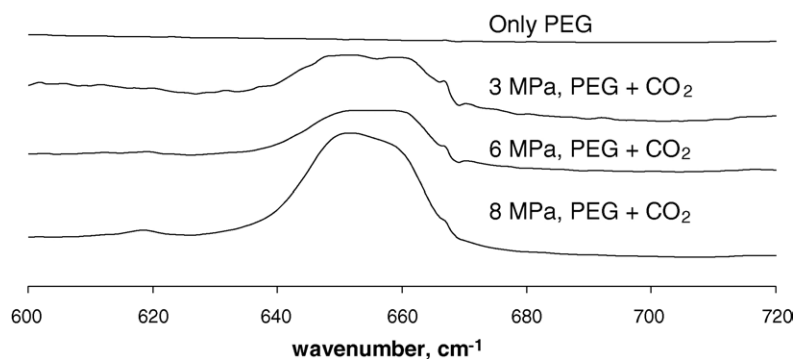


Fig. 10. The spectra of the bending vibrations of CO₂ entrapped in PEG.

The shifts of the C=O groups in P120 and P130 with the increasing CO₂ pressure are shown in Figs. 5 and 6. It was observed that the shifts for P120 are slightly higher than for P130. Since these two materials have the same chemical group (here shift of the carboxyl is considered) and nearly same thermal properties, we thought in first instance that the different behavior could be accounted for by the difference in the steric hindrance close to the carboxyl group. A schematic representation of the steric hindrance in the two cases is reported in Fig. 11. As can be seen, for P120, the presence of the methyl group in α position with respect to the C=O bond, dramatically increases the steric hindrance, thus making in principle the acid–base Lewis interaction with CO₂ much more difficult. In the case of P130, the methyl group is substituted with a hydrogen which of course displays much less hindrance for the interaction with CO₂. Obviously, since the observed shifts are actually higher for P120 (more hindrance) than P130 (less hindrance), other factor may play a more determining role. In this case, since the only other difference is the one regarding molecular weight (higher for P130 than for P120), we hypothesize that the difference in an accessible free volume in the polymers may be more important than the one caused by the steric hindrance. In polymers, effect of the MW on the free volume is generally observed in terms of the viscosity. The higher the MW the higher is the viscosity, i.e. the lower is the accessible free volume.

Thus, it is more difficult for CO₂ to access the C=O groups in P130. Shah et al. [19] have found that the accessible free volume of polymer has a greater effect on solubility than the CO₂–polymer interactions. However, individual contributions of these different factors to the shifts require in our opinion a detailed theoretical study.

The situation becomes even more complicated if one compares, for example, the shifts relative to the bending vibrations in the aromatic region, where no significant shifts could be observed for P120, P130 and PPO (all of these contain aromatic rings in the backbone). In this case, indeed, the shift differences between the three polymers are less than 0.3 cm^{−1}. The latter value is in our opinion too small to allow drawing conclusions on the reported behavior.

These data clearly show that the same chemical group, if present in polymers with different properties (molecular weight, thermal behavior, steric hindrance) result in different FT-IR shifts upon interaction with CO₂. In order to define a clear trend, theoretical simulation should be carried out to calculate ab initio the strength of the interaction.

Since the shifts obtained with the chemical groups on the polymers were small, we tried to determine the interaction strength by analyzing the bending vibrations of the CO₂ entrapped into the polymer. A nice correlation, as described in the literature [7,8] for other polymers, can be found when considering the bending vibrations of CO₂ entrapped into the

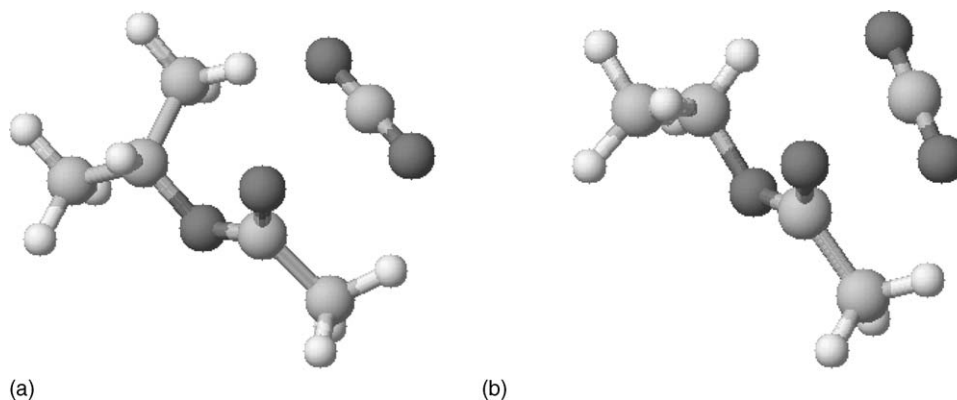


Fig. 11. Schematic representation of the steric hindrance for interaction of CO₂ with carboxyl groups in P120 (a) and P130 (b). Gray: C, white: H, black: O.

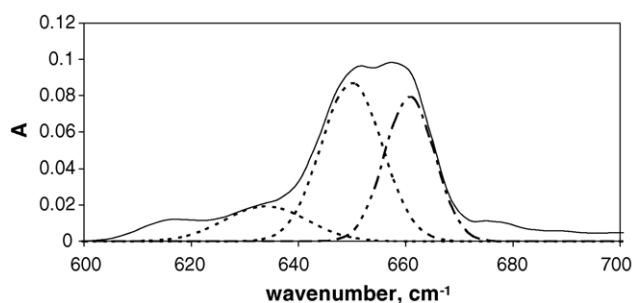


Fig. 12. The deconvolution of CO₂ absorption band in PEG.

polymer. The width of the ν_2 absorption band of CO₂ corresponding to a weak interaction with the polymer was used to estimate the strength of interaction. Similar to our results, absence of the splitting of CO₂ band in the ν_2 mode for polymers and PYR containing phenyl rings has been reported. However, Meredith et al. [8] have deconvoluted the CO₂ band in the ν_2 mode considering the contribution of the in-plane bending mode and out-of-plane bending mode as reported in the literature [7]. In case of PMMA such splitting has already been observed, as it does not contain a phenyl ring [7]. As expected, a better split could be observed in the ν_2 mode region at 6 MPa in case of PEG.

For the absorption band around 660 cm⁻¹, it was possible to deconvolute (see Fig. 12 for PEG as example) the experimental spectrum in different contributions: one located at about 650 cm⁻¹, the other at about 660 cm⁻¹. The bands around 650 and 660 cm⁻¹ are actually assigned to the bending vibration of CO₂ (in-plane bending and out-of-plane modes, respectively), which form a doublet. Despite the lack of an evident splitting in the CO₂ band, it is also possible to deconvolute the spectra of the other polymers by estimating the two peaks around 650 and 660 cm⁻¹ as reported by Meredith et al. [8]. Here, only the widths of the total bands (Table 2), i.e. without splitting, are considered. The widths are reported for 6 MPa, since the considerable shifts were observed in the chemical groups of the polymers at this pressure. If one compares different materials (by comparing again the band width), it is then possible to rank them according to their interaction strength with CO₂:

PEG \approx PPO \gg P120 \approx P130

The rank above is clearly reflective of the chemical structure: ether groups (PEG, PPO) interact stronger than carboxyl one (P120, P130). A similar ranking was observed at 3 MPa.

Table 2
Deconvolution data for all polymers

Polymer	Pressure (MPa)	Width (cm ⁻¹)	Wavenumber (cm ⁻¹)
PPO	6	8.2	658.8
P120	6	6.0	653.9
P130	6	6.1	653.2
PEG	6	8.6	652.1

Ideally, one would like to compare this rank with the solubility of CO₂ into the polymer, expecting a higher solubility according to the rank. Beckman and co-workers have reported strong CO₂ interactions for polymers with ether functionalities [20].

The effect of CO₂ solubility on the T_m or T_g depression could also be observed in the FT-IR studies depending on the enhancement in the free volume. As an example one may compare spectrum of PEG and PPO at 8 MPa (Figs. 2 and 9). Spectrum of PPO is basically the same as the one at 3 and 6 MPa, i.e. no significant differences are observed in the transition from sub-critical to supercritical CO₂. On the contrary, the shape of the PEG spectrum changed completely, probably because of the larger enhancement of the free volume as T_m was reduced in the presence of CO₂. In addition, despite of a similar T_g such results were not observed with P120 and P130. It can also be related to the smaller free volume available in P120 and P130.

4. Conclusions

FT-IR equipment can be conveniently modified to work under elevated CO₂ pressures. Shift of FT-IR absorption bands of the polymer is indicative of interaction between the polymers and CO₂ but only on a qualitative level. This close interdependence of the shift both on the pressure and the kind of material is confirmed by the absorption bands of CO₂ itself. Analysis of the band width allows ranking the polymers containing different chain groups according to their interaction strength with CO₂. The interaction strength was higher in the polymers containing ether group than the polymers containing ester group. A correlation between FT-IR spectra and solubility of CO₂ is not possible just on the basis of the shifts for the chain groups of polymers containing a similar chemical structure. Free volume effects must be taken into account. Theoretical simulation is needed to properly distinguish the different effects and possibly obtain a more quantitative correlation between FT-IR and solubility data. Shifts are dependent on structure of chemical group, thermal property of the polymer (T_g or T_m) and in general free volume effects (indeed same chemical groups in different polymers give different shifts).

Acknowledgments

This research is supported by the Technology Foundation STW, Applied Science Division of NWO and the Technology Programme of the Ministry of Economic Affairs.

References

- [1] A.I. Cooper, Synthesis and processing of polymers using supercritical carbon dioxide, *J. Mater. Chem.* 10 (2000) 207–234.

- [2] J.L. Kendall, D.A. Canelas, J.L. Young, J.M. DeSimone, polymerizations in supercritical carbon dioxide, *Chem. Rev.* 99 (1999) 543–564.
- [3] D.L. Tomasko, H. Li, D. Liu, X. Han, M.J. Wingert, L.J. Lee, K.W. Koelling, A review of CO₂ applications in the processing of polymers, *Ind. Eng. Chem. Res.* 42 (2003) 6431–6456.
- [4] J.R. Fried, W.J. Li, High-pressure FTIR studies of gas-polymer interactions, *J. Appl. Polym. Sci.* 41 (1990) 1123–1131.
- [5] B.J. Briscoe, C.T. Kelly, Optical studies of polymers in high pressure gas environments, *Mater. Sci. Eng.* A168 (1993) 111–115.
- [6] S.G. Kazarian, M.F. Vincent, C.A. Eckert, Infrared cell for supercritical fluid-polymer interactions, *Rev. Sci. Instrum.* 67 (1996) 1586–1589.
- [7] S.G. Kazarian, M.F. Vincent, F.V. Bright, C.L. Liotta, C.A. Eckert, Specific intermolecular interaction of carbon dioxide with polymers, *J. Am. Chem. Soc.* 118 (1996) 1729–1769.
- [8] J.C. Meredith, K.P. Johnston, J.M. Seminario, S.G. Kazarian, C.A. Eckert, Quantitative equilibrium constants between CO₂ and Lewis bases from FTIR spectroscopy, *J. Phys. Chem.* 26 (1996) 10837–10848.
- [9] N.M.B. Flichy, S.G. Kazarian, C.J. Lawrence, B.J. Briscoe, An ATR-IR study of poly(dimethylsiloxane) under high-pressure carbon dioxide: simultaneous measurement of sorption and swelling, *J. Phys. Chem. B* 106 (2002) 754–759.
- [10] S.G. Kazarian, Polymers and supercritical fluids: Opportunities for vibrational spectroscopy, *Macromol. Symp.* 184 (2002) 215–228.
- [11] S.G. Kazarian, K.L. Andrew Chan, FTIR imaging of polymeric materials under high-pressure carbon dioxide, *Macromolecules* 37 (2004) 579–584.
- [12] Y.-T. Shieh, K.-H. Liu, The effect of carbonyl group on sorption of CO₂ in glassy polymer, *J. Sup. Fluids* 25 (2003) 261–268.
- [13] N.J. Harrick, *Internal Reflection Spectroscopy*, Harrick Scientific Corp., Ossining, NY, 1987.
- [14] A.K. Dikshit, A. Kaito, Structure formation during the isothermal crystallization of an oriented blend of isotactic polystyrene with poly(2,6-dimethyl-1,4-phenylene oxide), *Macromol. Rap. Comm.* 25 (2004) 1019–1023.
- [15] B.J. Holland, J.N. Hay, The thermal degradation of PET and analogous polyesters measured by thermal analysis-Fourier transform infrared spectroscopy, *Polymer* 43 (2002) 1835–1847.
- [16] D.-H. Jung, Y.K. Ko, H.-T. Jung, Aggregation behavior of chemically attached poly(ethylene glycol) to single-walled carbon nanotubes (SWNTs) ropes, *Mater. Sci. Eng. C24* (2004) 117–121.
- [17] F.-Q. Nie, Z.-K. Xu, Q. Yang, J. Wu, L.-S. Wan, Surface modification of poly(acrylonitrile-co-maleic acid) membranes by the immobilization of poly(ethylene glycol), *J. Memb. Sci.* 235 (2004) 147–155.
- [18] E. Kukova, M. Petermann, E. Weidner, Phase behaviour (S-L-G) and fluiddynamic properties of high viscous poly(ethylene glycols) in the presence of compressed carbon dioxide, in: *Proceedings of 6th ISSF, Materials Processing*, vol. 3, 2003, pp. 1547–1552.
- [19] V.M. Shah, B.J. Hardy, S.A. Stern, Solubility of carbon dioxide, methane, and propane in silicone polymers. Effect of polymer backbone chains, *J. Polym. Sci.: Polym. Phys.* 31 (1993) 313–317.
- [20] T. Sarbu, T.J. Stranec, E.J. Beckman, Design and synthesis of low cost, sustainable CO₂-philes, *Ind. Eng. Chem. Res.* 39 (2000) 4678–4683.